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FLAVONOID PIGMENTS IN THE MARBLED WHITE BUTTERFLY (*MELANARGIA GALATHEA* SEITZ)

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In 1926, D.L. Thomson[1] isolated from the wings of the Marbled White butterfly (*Melanargia galathea*) a small amount of material which he considered to be quercetin. What appeared to be the same substance was extracted[2] from cocksfoot grass (*Dactylis glomerata*), a food plant of *galathea*. We have now re-investigated the flavonoid constituents of this insect and wish to report the results briefly: full details will be published in the *Journal of Insect Physiology*.

Flavonoid components are present in both wings and bodies. An ethanol extract of 400 Marbled Whites was banded on to sheets of Whatman 3mm paper and eluted with 15% acetic acid. Repeated chromatography with seven solvent systems revealed the presence of at least twelve flavonoid compounds, mostly glycosides. The main fraction was finally isolated as pale yellow micro needles (1 mg.), m.p. 285-290° (decomp.) (Kofler) identified as tricin by mixed m.p., identical ultraviolet and infrared (KBr) spectra, by the bathochromic shifts shown below, and by co-chromatography in seventeen solvents.

1 D.L. Thomson, *Biochem. J.* **20**, 73 (1926).

2 D.L. Thomson, *Biochem. J.* **20**, 1026 (1926).

Solvent		*M. galathea* pigment λ max (mμ)	Tricin λ max (mμ)
95% EtOH		245s, 270, 351	245s, 270, 351
"	+ NaOAc	236, 275, 400	236, 275, 400
"	+ {NaOAc, H_3BO_3}	270, 352	270, 352
"	+ NaOH	263, 413	263, 413
"	+ $AlCl_3$	279, 301, 356	279, 301, 356

Another component (A), R_f 0.37 in 15% acetic acid and 0.41 in n-butanol/acetic acid/water (4:1:5, v/v), was evidently a glycoside. It was not hydrolysed by treatment with β-glucosidase at 38° for 24 hr. but on refluxing with 2 N HCl for 30 min. partial hydrolysis occurred to give two aglycones, one of which was identified as luterin (orientin) by its ultraviolet absorption and chromatographic behaviour, tabulated below.

Solvent		*M. galathea* glycoside(A) λmax (mμ)	Aglycone of (A) λ max (mμ)	Luterin (orientin) λ max (mμ)	Luteolin λmax (mμ)
95% EtOH		258, 270, 350	257, 269, 353	258, 269, 353	255, 267s, 351
"	+ NaOAc[a]	272, 405	257, 269, 353	273, 395	270, 368
"	+ {NaOAc, H_3BO_3}	265, 373	262, 374	263, 375	260, 375
"	+ NaOH	276, 415-8	276, 410	276, 413	273, 410
"	+ $AlCl_3$	279, 362, 384	271, 358, 380	278, 300s, 358, 388	276, 360, 390

[a] Unreliable behaviour with NaOAc has been noted before.[3]

The aglycone was co-chromatographed with authentic luterin in the three solvents listed, and we are indebted to Dr. Margaret K. Seikel who confirmed their identity by co-chromatography in 15% acetic acid, BAW

3 M.K. Seikel and A.J. Bushnell, J. Org. Chem. 24, 1995 (1959).

and 60% isopropanol. The second aglycone, presumably lutonaretin, was present in insufficient quantity for comparison with authentic material.

R_f values[a]

Compound	15% HOAc	$PhOH/H_2O$[b]	60% isoPrOH
M. galathea glycoside (A)	0.37	0.65	0.77
Aglycone of (A)	0.21	0.48	0.49
Lutexin (orientin)	0.23	0.47	0.50
Lutonarin	0.59	0.56	0.54
Luteolin	0.10	0.77	0.84

[a] Whatman No. 1 paper at 19° ± 1°. [b] Phenol saturated with water

The other pigments were present only in traces. Several appear to be luteolin or possibly 5'-methoxyluteolin (tricetin 3'-O-methyl ether) derivatives, and one may be an isoflavone.

So far as we are aware this is the first time that flavones have been positively identified in the animal kingdom. Tricin has been isolated from wheat[4] (*Triticum dicoccum*), and lutonarin, which on hydrolysis yields the two C-glycosides lutonaretin and lutexin, occurs in barley[3] (*Hordeum vulgare*). It is becoming clear that glycoflavones are widely distributed in grasses[5] and it seems likely that the butterfly pigments originate in the food of the larvae.

We are extending our investigations to other species in which flavones may be present.[6]

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4 J.A. Anderson and A.G. Perkin, *J. Chem. Soc.* 2624 (1931).

5 J.B. Harberne, personal communication.

6 E.B. Ford, *Proc. Roy. Entomol. Soc.* (London) [A] **16**, 65 (1941).

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